

博士論文(要約)

Atomic structures and properties of interfaces in
fluorite type oxide materials

(蛍石型構造酸化物界面の構造と物性に関する研究)

馮 斌

論文の内容の要旨

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氏名 馮 斌

In the present thesis, grain boundaries (GBs) in fluorite type oxide materials of CeO_2 and Y doped ZrO_2 (YSZ), including atomic structures, segregation behaviors and GB physical properties are systematically studied.

CeO_2 and YSZ have been widely used as catalysts and electrolyte materials for solid oxide fuel cells. Using polycrystalline materials, it is widely reported that the GBs affect the overall material performances such as ionic conductivities using polycrystalline materials. Although some approximated models have been proposed to explain the effect of the GBs, only the averaged effect of GBs is available in most of these studies. The physics behind these GBs still remains unclear, such as the detailed atomic structure and local element distribution in GBs. In this study, we tried to analyze the role of the GBs in these two materials at atomic scale by the combination of scanning transmission electron microscopy (STEM) and theoretical calculations.

In Chapter 2, the atomic structure of CeO_2 $\Sigma 3$ GB was observed by STEM and the valance state of the Ce in the GB was determined from the electron energy loss spectroscopy (EELS). The Ce was found to keep 4+ in the GB as those in the bulk, which demonstrates that there are no oxygen vacancies in this GB. These experimental approaches were also in good agreement with the GB structure predicted by the static lattice calculations and the density functional theory (DFT) calculations. This result is different from the $\Sigma 5$ GB reported previously, of which the GB structure

was more stable with oxygen vacancies. These results suggested that the GB oxygen nonstoichiometric behavior in CeO₂ might be dependent on the GB characters.

Thus in Chapter 3, the effect of the GB characters on the atomic structures and oxygen nonstoichiometric behavior was analyzed systematically using five model GBs with different rotation axis and GB planes. The oxygen vacancy content was estimated from the valence state of Ce determined by the EELS analysis. Then the same theoretical approaches with the previous chapter were carried out. In the GB modeling, oxygen vacancies were introduced in each GB and the amount of oxygen vacancies introduced was determined from the EELS results. It is shown that all the GB structures predicted by the calculations agree well with the atomic configurations obtained from STEM images. Therefore the GB structures were determined in atomic scale with the precise information of oxygen vacancy content. The origin of such GB oxygen nonstoichiometric behavior was further revealed. It is shown that the oxygen coordination deficient sites are formed in the GB. Such densities were calculated and used as parameter to evaluate the GB structural distortions. The oxygen vacancy concentrations are highly dependent on the GB atomic structures due to local structural distortions: the more the GB is distorted, the more the oxygen vacancies form. By introducing oxygen vacancies, such distortions are relaxed and the GB tends to be more stable. As a result, oxygen nonstoichiometric GBs were formed. In this way, the GB dependence oxygen nonstoichiometric behavior was clarified.

In Chapter 4, local GB properties were analyzed. GB oxygen reaction activities were measured at nano-scale by the electrochemical strain microscopy (ESM). It is revealed that the GB reactivity is stronger than that of the bulk in the $\Sigma 5$ GB, in which the oxygen vacancy density is the largest among the five model GBs. For the other GBs, no obvious reactivity change is attained compared with the bulk. Thus we conclude that GB oxygen vacancy concentrations critically affect the corresponding GB oxygen reactivity. In summary, a simple and clear GB structure-property relationship was established.

In Chapter 5, energy dispersive x-ray spectroscopy (EDS) analysis was carried out to investigate the local defect chemistry near the GBs, as well as the atomic-scale Y segregation behavior in the GBs. The segregation behavior and the GB ionic conductivity drop in YSZ GB have been widely discussed by the classical space charge theory. However, the element distribution near the GB, especially for oxygen content, is still under debate. In this study, element concentrations near the GBs are directly mapped by STEM-EDS. Since GBs have unique atomic configurations different from the perfect crystal, element concentrations were discussed instead of the absolute intensities. It was revealed that the Y concentrations are always higher in the GB; while the oxygen concentrations increased in the GB for all the model GBs analyzed except for the $\Sigma 3$ GB. The effect of electron channeling was also taken into account since it was known that such effect is critical for STEM-EDS quantification. EDS simulation based on the multislice method was carried out, and the electron

channeling was discussed. By these approaches, it is concluded that the increase of oxygen concentration in the GB originates from the material itself rather than the artifact from the EDS measurement. These results agree well with the defect chemistry predicted by the space charge theory.

It was found that the oxygen concentration is only decreased in the $\Sigma 3$ GB, but Y still segregated in this GB. These results are inconsistent with the space charge theory, suggesting that other segregation mechanisms exist at least for this GB. Then EDS mapping were taken in the GB at atomic scale and the Y segregation sites were directly determined. Y atoms were confirmed to be segregated in the preferred sites in the $\Sigma 3$ GB, while there is not any preferred segregation sites in the other model GBs with periodicity. In order to understand such segregation mechanisms, Monte Carlo (MC) simulation were carried out for the $\Sigma 3$ GB and the $\Sigma 5$ GB as a comparison. The amount of Y was systematically increased in the calculation in order to simulate the segregation process. The calculated results showed good agreement with the experimental results for both of the GBs, indicating that such complex GB segregation behavior could be predicted using MC simulations. By analyzing both the atomic structure and corresponding segregation energy for different Y concentration, a detailed segregation process is described for the $\Sigma 3$ GB: The Y would first segregate for elastic effect of relaxing the local strain in the GB. Further segregation driving force comes from the Coulombic interactions and a new ordered phase was formed in the bulk part near the GB. Such driving force is likely to be valid for all the GBs. In this way, we discussed the space charge theory from both the oxygen distributions and Y segregation mechanisms in the end. The present study provides essential viewpoint for the fundamental physics in ceramic interfaces.

A brief summary was presented in Chapter 6. In this study, we systematically analyzed the complex structure and properties in the GBs of CeO_2 and YSZ in atomic scale, providing critical information that difficult to be obtained from the traditional macroscopic studies. The present study is essential for the understanding of fundamental physics in ceramic GBs, as well as material designing strategy innovations for industry in near future.